# Emission Properties and Use of Multinuclear $Cu_nS_m$ Clusters within Aromatic Micelles

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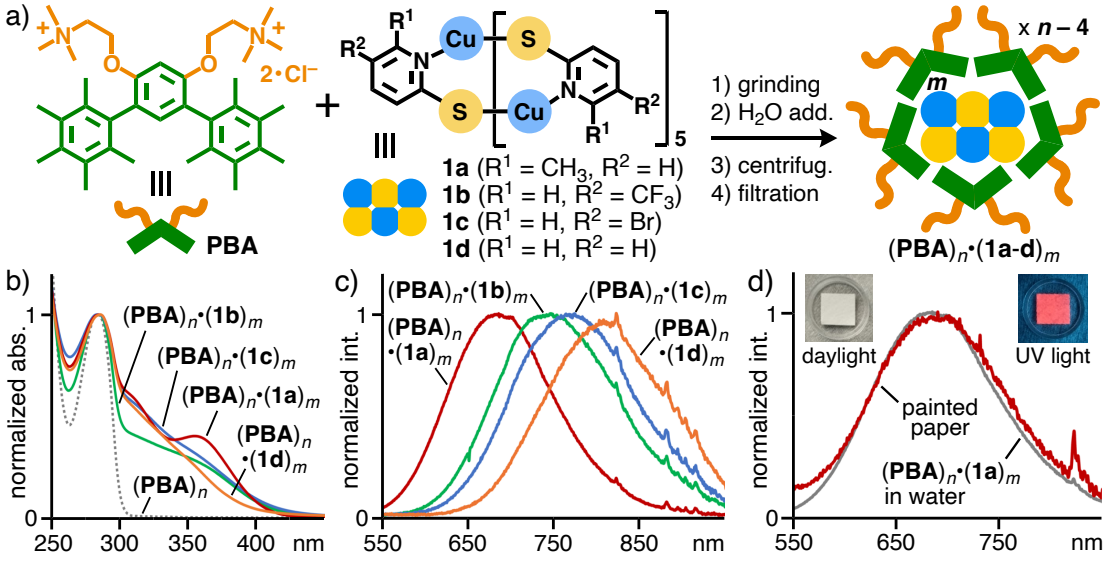
**Keywords**: Multinuclear Copper-sulfur Cluster; Aromatic Micelle; Encapsulation; Red-to-NIR Emission; Security Ink

Multinuclear $Cu_nS_m$ clusters have been attracted interest, due to their characteristic photophysical properties.[1] However, the majority of $Cu_nS_m$ clusters are insoluble and/or unstable in organic solvents as well as in water, which interferes with their applications. Aromatic micelle displays wide-ranging host ability toward aromatic compounds as well as metal-complexes.[2] On the other hand, its encapsulation ability toward multinuclear $M_n$ clusters ($n > 3$) has not been unrevealed to date.

Here we report the solution-state red-to-near-infrared (NIR) emission of $Cu_6S_6$ clusters upon encapsulation by aromatic micelles in water. The resultant solution served as potential security ink. $Cu_6S_6$ cluster **1a-d** were efficiently incorporated by aromatic micelle $(\mathbf{PBA})_n$ in water through a grinding method (Fig. a). The UV-visible spectra of the resultant solutions showed new absorption bands derived from **1a-d** ($\lambda$ = 300-420 nm; Fig. b), indicating their water solubilization upon encapsulation. Host-guest complexes $(\mathbf{PBA})_n\bullet(\mathbf{1a\text{-}d})_n$ displayed various red-to-NIR emission in water, depending on the substituents on the clusters ($\lambda_{max}$ = 685-805 nm; $\phi$ = 16-31%; Fig. c). The aqueous $(\mathbf{PBA})_n\bullet(\mathbf{1a})_n$ solution was used as writing and painting ink on paper, which is colorless under daylight yet red-to-NIR emissive under UV-light irradiation (Fig. d). Furthermore, this protocol was applicable to $Cu_{12}S_6$ and $Cu_4I_4$ clusters.




[1] A. Baghdasaryan, T. Bürgi, *Nanoscale* **2021**, *13*, 6283–6340. [2] M. Yoshizawa, L. Catti, *Acc. Chem. Res.* **2019**, *52*, 2392–2404.